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(54) General-purpose cleaning compositions.

(57) A general purpose cleaning composition comprises 0.01 to 90% by weight of a nonionic surfactant, 0.005 to 50% by weight of a cationic surfactant which has a sanitising action, and 0.003 to 20% by weight of a non-anionic polymer which has an adsorptive affinity to hard surfaces. The inclusion of the non-anionic polymer in general-purpose cleaners containing a nonionic and a cationic detergent provides a significant streak free benefit in the cleaned surfaces.

**EP 0 342 997 A2**

## Description

## GENERAL-PURPOSE CLEANING COMPOSITIONS

The present invention relates to general-purpose cleaning compositions with improved properties. More particularly, it relates to general-purpose cleaning compositions which have a sanitizing effect and a streak-free cleaning benefit.

General-purpose cleaning compositions are compositions which are intended for use in the cleaning of hard surfaces, such as tiles, walls, floors, kitchen furniture, glass, plastic/covered doors, etc. Such general-purpose cleaning compositions are well known in the art and have found substantial commercial use.

These compositions are usually provided in the form of a particulate composition, from which the user prepares an aqueous solution, or in the form of a liquid composition which contains a suitable solvent, such as water, or a mixture of these. These liquids can be applied either neat for the removal of stubborn stains, or in the form of a more diluted solution for large surface area cleaning.

However, despite the fact that many of such general-purpose cleaning compositions often satisfactorily remove soil and dirt from hard surfaces, they often leave behind residues once the solvent medium has evaporated during the drying of the cleaned surface. The surface presents residues, visible as dull streaks, instead of the bright, shining surface that the consumer wants to see.

It is therefore an object of the present invention to provide general-purpose cleaning compositions with a "streak-free" cleaning benefit, i.e. after cleaning a hard surface with such a cleaning composition, the hard surface, when dry, does not show a residue in the form of visible, dull streaks to any significant degree.

For brevity's sake, such a cleaning composition will hereafter be called a streak-free, general-purpose cleaning composition, "streak-free" being understood as described hereabove.

Frequently, an important aspect of general-purpose cleaners is that they should not only satisfactorily clean hard surfaces, but also sanitize the hard surfaces to render them hygienic. This has been recognized in the art, and many proposals concerning such cleaning compositions, often referred to as detergent sanitizers, have been made (see e.g. "Surface Active Ethylene Oxide Adducts" by N.Schönfeldt, Pergamon Press, 1969, pages 439-441). Such compositions are mainly based on a mixture of nonionic and cationic detergent surfactants although cationic alone can be used.

A disadvantage of such detergent sanitizers based on a mixture of nonionic and cationic detergent surfactants is that they frequently give rise to streak formation on the surfaces when dry, which, as explained above, is unattractive to the consumer.

It is therefore an object of the present invention to provide a general-purpose cleaner having a sanitizing effect, containing a mixture of a nonionic and a non-anionic detergent surfactant, which also provides a streak-free cleaning benefit.

In our European Patent 0 066 342, published on 30 December 1986, we have described and claimed a streak-free, general-purpose cleaning composition comprising a nonionic detergent surfactant and an at least partially alcohol-esterified resin. However, the inclusion of such partially esterified resins in a composition which also contains a cationic detergent surfactant does not provide a streak-free benefit, but can rather give rise to worse streak formation.

We have now surprisingly found that the inclusion of a non-anionic polymer in general-purpose cleaners which contain a mixture of a nonionic and a cationic detergent surfactant significantly reduces streak formation and also provides an improved, streak-free cleaning benefit.

The invention will further be described below in its essential details.

The nonionic detergent surfactant used in the present invention can be any suitable type of nonionic detergent known. Basically, nonionic detergent surfactants consist of a hydrophobic moiety, such as a C<sub>8</sub>-C<sub>20</sub> fatty acid amide, and a hydrophilic moiety which consists of alkylene oxide units. These nonionic detergent surfactants are, for instance, alkoxylation products of the above hydrophobic moieties containing from 2 to 30 moles of alkylene oxide. As alkylene oxides, ethylene, propylene and butylene oxides and mixtures thereof are used.

Typical examples of such nonionic detergents are C<sub>9</sub>-C<sub>11</sub> primary, straight chain alcohols condensed with from 4-9 moles of ethylene oxide, C<sub>12</sub>-C<sub>15</sub> primary straight chain alcohols condensed with 6-12 moles of ethylene oxide, or with 7-9 moles of a mixture of ethylene oxide and propylene oxide, C<sub>11</sub>-C<sub>15</sub> secondary alcohols condensed with from 3-15 moles of ethylene oxide, and C<sub>10</sub>-C<sub>18</sub> fatty acid diethanolamides. Further examples of nonionic detergent surfactants may be found in M.Schick's textbook "Nonionic Surfactants", M.Dekker Inc., New York, 1967. Mixtures of various nonionic surfactants may also be used. Tertiary amine oxides, such as higher alkyl di(lower alkyl) amine oxides, e.g. lauryl dihydroxyethyl amine oxide, may also be used as a suitable nonionic surfactant.

Nonionic detergent surfactants known in the art as "topped" or "peaked" nonionic detergent surfactants are also useful in the present invention. Topped nonionic detergent surfactants can be made by subjecting the usual nonionic detergent surfactant to a steam distillation treatment, by which the free and low alkoxylation alcohol can be removed, and peaked nonionic detergent surfactants can be made by carrying out the alkoxylation with special catalysts, which results in products with a much sharper peak in the alkoxylation distribution. Topped nonionic detergent surfactants are e.g. described in US Patent Specification 3 682 849.

Topped or peaked nonionic detergent surfactants suitable for the present invention contain an average

number of alkylene oxide units of between 3 and 15, preferably between 4 and 12, per molecule of the hydrophobic moiety, i.e. a C<sub>6</sub>-C<sub>18</sub> primary or secondary, straight or branched chain alcohol, and preferably contain less than 2% by weight of non-alkoxylated alcohol, and less than 4% by weight of mono-alkoxylated alcohol. Particularly suitable are nonionic detergent surfactants with these specifications and prepared from C<sub>11</sub>-C<sub>15</sub> linear primary alcohols condensed with 7-11 moles of ethylene oxide, C<sub>9</sub>-C<sub>11</sub> oxo-alcohols condensed with 5 moles of ethylene oxide, and C<sub>6</sub>-C<sub>10</sub> linear primary alcohols condensed with 4-5 moles of ethylene oxide.

For optimum detergency, the shorter alkyl chain length nonionic surfactants are preferred, particularly when the degree of alkoxylation is relatively low. Thus, the alkoxyated C<sub>9</sub>-C<sub>11</sub> alcohols are preferred to the correspondingly alkoxyated C<sub>12</sub>-C<sub>15</sub> alcohols, and the C<sub>9</sub>-C<sub>11</sub> alcohols condensed with 5 moles of ethylene oxide are preferred to the same alcohols but condensed with 8 moles of ethylene oxide.

In general, when dissolved in water, the HLB-value of the nonionic surfactant or mixture of nonionic surfactants should lie between 10 and 15. Nonionic surfactants with an HLB-value of below 11 are generally not soluble in water to any appreciable extent without another active detergent present, but it is possible to dissolve higher levels of such low HLB-nonionic surfactants in mixtures of water and an organic solvent.

For optimum streak-free results, the nonionic surfactant should preferably provide a cloud point of the aqueous solution of the final composition above the temperature of normal use of the diluted solution.

This can be achieved by a proper choice of the type of nonionic surfactant or mixtures of various nonionic surfactants or by the co-use of another detergent surfactant, such as an anionic or amphoteric surfactant.

From 0.01 to 90% by weight with respect to the final composition of one or more nonionic surfactants will be present in the final composition. Usually, this amount will range from 0.1 to 30% by weight, and it has been found that at least 1% should be present to obtain both a reduced streaking and an improved cleaning effect. Preferably therefore, the amount of nonionic detergent surfactant will range from 1% to 30%, and especially preferably from 1% to 10% by weight of the final composition.

The cationic detergent surfactant to be used in the present invention can be any cationic detergent surfactant with a sanitizing action well known in the art. Examples of such cationic detergent surfactants are the quaternary ammonium compounds, such as the mono- or di(long chain alkyl) tri- or di(short chain) alkyl quaternary ammonium salts; mono- or di(long chain alkyl) imidazolinium compounds; substituted long chain alkyl polyamine salts; alkyl pyridinium salts and so on. Further suitable examples can be found in Schwartz, Perry and Berch, Vol.II (1958), "Surface-active Agents and Detergents" under the heading "Cationic Surface Active Agents".

Specific examples of suitable cationic detergent surfactants are the long chain (C<sub>8</sub> and higher) alkyldimethylbenzylammonium chlorides (e.g. the commercial product Dodigen ex American Hoechst Corp.), the alkyl (C<sub>12</sub> and higher) trimethylammonium chloride, tetradecyl pyridinium chloride, alkyl (C<sub>12</sub>-C<sub>16</sub>) trimethylammonium bromide, di-isobutyl-phenoxy-ethoxyethyl dimethylbenzylammonium chloride. Quaternary phosphonium and sulphonium compounds can also be used. These examples are, however, not limiting the scope of the invention; other detergent surfactants with a sanitizing action can be suitably used.

In general, the amount of cationic detergent surfactant used in the present invention ranges from 0.005 to 50%, usually from 0.1 to 15%, and preferably from 0.25 to 5% by weight.

The non-anionic polymer to be used in the present invention should have an adsorptive affinity to the hard surface and should be hydrophilic. Preferably, it should bear a positive charge on its molecular structure (either as such or under the conditions of use), and consequently cationic polymers are clearly preferred to nonionic polymers.

Suitable cationic polymers for use in the present invention are those which adsorb on to the hard surface at least as quickly as, and preferably, more quickly than, the cationic detergent surfactant.

Typical examples of such cationic polymers are Busan 77 (ex Buckman) which is a poly[oxyethylene (dimethyliminio) ethylene (dimethyliminio) ethylene dichloride] with a polymerization degree of about 20, Busan 79 (ex Buckman) which is a poly [hydroxy-ethylene (dimethyliminio) ethylene (dimethyliminio) methylene dichloride], Busan 1055 (ex Buckman) which is a poly[2-hydroxyethylenedimethyliminio-2-hydroxy-propylenedimethyliminio methylene] dichloride and structurally related cationic polymers such as 4/polyethylene glycol ionene bromides where the molecular weights of the PEG portion are 6000 and 1500 respectively, Zetag 57 and Zetag 87 which are high molecular weight cationic acrylamides ex Allied Colloids, Merquat 100 which is a polydimethyldiallylammonium chloride ex Merck, Mirapol A15 which is a poly[N-(3-dimethylammonio)propyl]-N [3-(ethyl-eneoxyethylene dimethylammonio)propyl] urea dichloride with a polymerisation degree of about 6 and homopolymer 78-4396 ex National Starch which is poly(dimethyldiallyl ammonium chloride).

Particularly preferred cationic polymers for use in the present invention are Busan 77 (ex Buckman) Merquat 100 (ex Merck) and Mirapol A15 (ex Miranol).

Examples of suitable nonionic polymers are Jaguar HP 8 and HP60 (ex Meyhall), which are nonionic substituted hydroxypropyl guar gums, and polyvinylpyrrolidones and poly(2-vinylpyridines) which are especially suitable for very low pH compositions. However, as said above, the cationic polymers are clearly preferred to the nonionic polymers.

It has been found that contact angle measurements may provide a guide as to the suitability of non-anionic polymers for use in the composition. In particular low contact angles are an indication of suitability. The contact angle is measured as the receding angle of a drop of water (approximately 0.4cm<sup>3</sup> forced to spread by tilting

movements on a horizontal black ceramic tile which has been previously treated with a formulation comprising 1.5% C<sub>8</sub>-C<sub>18</sub> alkyl dimethylbenzylammonium chloride, 1.2% C<sub>11</sub> alkyl polyoxyethylene (3EO), 0.6% C<sub>8</sub>-C<sub>11</sub> linear alcohol condensed with 5 moles of ethylene oxide and 0.8% by weight of the non-anionic polymer, and then allowed to dry. Preferably the non-anionic polymers have contact angles of less than 15° and more preferably less than 10°. However, such measurements can only be used as a guide. Some polymers moreover are not soluble at the levels of the above test and yet still give a streak free benefit.

A more reliable guide to suitable non-anionic polymers is provided by an adsorption test which, by way of surface tension measurements, determines the adsorptive affinity of the non-anionic polymer compared to that of a typical cationic surfactant when the components are in competition for an "ideal" surface such as colloidal silica. The adsorption test comprises the following steps:

(i) 10g of a 0.015% solution of the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) is placed in a tensiometer vessel and equilibrated to 25°C. The surface tension is measured.

(ii) 100 microlitres of a 1% solution in distilled water of the non-anionic polymer is pipetted into the CTAB solution and mixed thoroughly. The surface tension is measured again.

(iii) 30 microlitres of an aqueous colloidal silica solution (Ludox HS-40) is pipetted into the solution and mixed thoroughly. The surface tension is then measured at timed intervals.

The quantity of silica added is chosen so that the non-anionic polymer and the surfactant must compete for adsorption sites. It has been found that the preferred cationic polymers according to the invention cause a less than 15 dyne change in surface tension when tested according to the adsorption test defined above, particularly preferred cationic polymers cause a less than 10 dyne change in surface tension according to the adsorption test.

The amount of non-anionic polymer in the compositions of the invention may range from 0.003 to 20%, usually from 0.01 to 15%, and preferably from 0.1 to 5% by weight.

It has been found that particularly preferred formulations of the invention have ratios of cationic surfactant: non-anionic polymer within the range 150:1 to 0.3:1 and most preferably 15:1 to 1:2.

The compositions may furthermore contain optional ingredients, such as preservatives, bactericides, bleaching agents, enzymes, thickening agents, colouring agents, perfumes, alkaline materials, sequestering agents, solvents and the like. They may also contain particulate abrasive, such as particulate calcite, to form an abrasive cleaning composition. They may be made in any physical form, such as powders, blocks, aqueous and non-aqueous liquids etc. Preferably, they are in liquid form, the balance of the formulation being an aqueous or non-aqueous medium. They may be applied as such, i.e. neat, or they may be made up into a solution before use to a concentration of generally 0.1 to 10%.

In general the streak-free benefit is independent of the pH of the composition. An exception is a polymer such as poly(2-vinylpyridine) in which case a composition of very low pH is necessary for optimum streak-free results to be obtained.

The invention will further be illustrated by way of Example.

#### EXAMPLE 1

The streak-free benefits of cationic polymers were tested as follows:

1. A solution of 0.5-1% of polymer in an aqueous liquid containing 1.5% (C<sub>12</sub>-C<sub>16</sub>) alkylbenzyl dimethyl ammonium chloride, 4% nonylphenol condensed with 8.5 moles of ethylene oxide, 0.3% perfume, balance water is prepared.

2. A quarter of a sponge cloth is cut; it is rinsed with plenty of tap water of average hardness (ca. 12 degrees French Hard) and then gently squeezed.

3. Ten drops of the solution are dropped on the sponge cloth.

4. A single black ceramic tile is washed with this sponge and, after rinsing the sponge cloth, wiped again.

5. Then the tile is left to dry naturally.

The streak-free benefit is then assessed visually. The following results were obtained:

Polymer used:                      Streak-free benefit  
Nonionic polymers

Polyvinyl pyrrolidone (K 90 ex GAF)	Slightly streaky	5
Hydroxypropyl guar (Jaguar HP 8)	Slightly streaky	
<u>Cationic polymers</u>		
Jaguar C13 (ex Meyhall)	No benefit	10
Jaguar C15 (Ex Meyhall)	No benefit	
Merquat 550 (ex Merck)	No benefit	
Polymer JR 400 (ex Union Carbide)	No benefit	
Mirapol A15	Very slightly streaky	15
Celquat L 233	Very slightly streaky	
Homopolymer DMDAAC	Very slightly streaky	
Merquat 100	No streaks	20
Busan 77	No streaks	

EXAMPLE 2

The following formulation containing: 25

1.5% C<sub>12</sub>-C<sub>16</sub> alkyldimethyl benzyl ammonium chloride

1.2% C<sub>11</sub>-C<sub>13</sub> oxo-alcohol condensed with 3 moles of ethylene oxide

0.6% C<sub>9</sub>-C<sub>11</sub> linear alcohol condensed with 5 moles of ethylene oxide

q.s. water 30

also containing

0.6% (A) or 0.9% (D) Busan 77, or 0.6% (C) resp. 0.8% (B) Merquat 100

was tested and compared with the formulation of Example 1 (without polymer) as control.

The following results were obtained.

a. Soil removal (triolein + carbon black) 35

Control	50%	
A	52.5%	
B	52%	
C	46.9%	40
D	52.6%	

## b. 45

Streaking test    diluted in hard    neat  
                          water (40° FH)  
                          45° C

Control	Streaky	Very streaky	50
A	Slightly streaky	Not streaky	
B	Not streaky	Not streaky	
C	Not streaky	Not streaky	
D	Not streaky	Not streaky	55

60

65

c. Logarithm of bacteria survivors in solutions  
(1:20 dil.) (solution containing  $10^7$  bacteria/cm<sup>3</sup>)

		after 10'	after 30'	after 2 hrs
5	Control	4.0	3.7	3.3
	A	5.5	4.6	3.6
	B	3.9	3.8	3.5
	C	3.9	3.7	3.4
10	D	5.4	5.0	4.1

d. Logarithm of bacteria survivors on cloth (1:10  
dil.) (dish cloths contaminated, contacted for 30  
seconds with the solution)

		after 2 hrs	after 24 hrs
20	Control	5.7	6.5
	A	4.2	5.6
	B	2.2	5.4
	C	3.4	5.8
25	D	5.9	5.9

#### EXAMPLE 3

The following formulation is a liquid abrasive cleaning composition with an improved streak-free benefit.

	%
30	
Topped C <sub>8</sub> -C <sub>11</sub> alcohol condensed with 5 moles of ethylene oxide	4.8
35	
C <sub>12</sub> -C <sub>16</sub> alkyldimethylbenzyl ammonium chloride	1.5
Particulate calcite	45.0
Nonionic polymer	0.4
40	
(Jaguar HP-8)	
Perfume	0.2
Water	balance

#### EXAMPLE 4

The adsorptive affinity of a range of non-anionic polymers was determined by the following adsorption test.

##### Adsorption test method

The adsorption test comprises the following steps:

(i) 10g of a 0.015% solution of the cationic surfactant CTAB is placed in a tensiometer vessel and equilibrated to 25°C. The surface tension is measured as approximately 51 dynes.

(ii) 100 microlitres of a 1% solution in distilled water of the non-anionic polymer is pipetted into the CTAB solution and mixed thoroughly. The surface tension is again measured. A value close to 51 dynes suggests that any interaction between the polymer and the surfactant is negligible.

(iii) 30 microlitres of an aqueous colloidal silica solution (Ludox HS-40) are pipetted into the solution and mixed thoroughly. The surface tension is then measured at timed intervals.

The non-anionic polymer from (ii) above was then incorporated in the following composition.

1.5% Alkyl (C<sub>8</sub>-C<sub>18</sub>) benzyldimethylammonium chloride  
1.2% Alkyl (C<sub>11</sub>) polyoxyethylene (3EO)  
0.6% Alkyl (C<sub>9</sub>-C<sub>11</sub>) polyoxyethylene (5EO)  
0.8% Non-anionic polymer  
balance water to 100%

The formulation was tested both neat and dilute as follows:

(a) Neat: 2g of the formulation were placed on a clean folded sponge cloth and wiped over a clean, dry,

vertical, black ceramic tile board. The cloth was then rinsed in demineralised water and the board wiped again before being left to dry naturally.

(b) Dilute: 4g of the formulation were diluted to 400g using 40° FH water at 45° C. A clean folded sponge cloth was immersed in the liquid, squeezed gently and wiped over the tile board. The cloth was then re-immersed, squeezed until damp and wiped over the tile board. The board was left to dry naturally.

The following results were obtained:

Polymer	Surface tension (dynes)			Effect	
	1	2	Time (Minutes)	Neat (a)	Dilute (b)
Busan 77	49.5	49.3	49.0	Streak Free	
Busan 79	55.4	55.3	54.9	Streak Free	
Busan 1055	52.8	52.7	52.2	Streak Free	
Merquat 100	58.6	58.1	57.4	Streak Free	
Mirapol A15	50.3	49.9	49.7	Streak Free	
Merquat 550	66.5	65.8	65.5	Very Streaky	
JR 125	67.3	66.5	65.2	Very Streaky	
PVP K90	67.9	67.2	66.8	Very Streaky	

JR 125 is a cationic substituted hydroxyethylcellulose ex Union Carbide. PVP K90 is a polyvinylpyrrolidone ex GAF.

None of the above polymers showed surface activity when added to distilled water. Little or no change in surface activity resulted from the addition of polymer to surfactant (i.e. little or no change in surface tension from step (i) to step (ii)). The results of the adsorption test correlate well with the streak free benefit for cationic polymers having a change in surface tension (when silica is added to a solution comprising surfactant and polymer according to the adsorption test as define above) of less than about 15 dynes and preferably less than about 8 dynes.

#### Claims

1. A general purpose cleaning composition comprising:
  - (a) 0.01 to 90% by weight of a nonionic surfactant;
  - (b) 0.005 to 50% by weight of a cationic surfactant which has a sanitising action;
  - (c) 0.003 to 20% by weight of a non-anionic polymer which has an adsorptive affinity to hard surfaces.
2. A composition as claimed in claim 1 wherein the non-anionic polymer (c) is a cationic polymer.
3. A composition as claimed in claim 1 or claim 2 wherein the nonionic surfactant is a topped nonionic.
4. A composition as claimed in any preceding claim wherein the composition comprises from 1 to 30% by weight of (a).
5. A composition as claimed in any preceding claim wherein the composition comprises from 0.1 to 15% by weight of (b).
6. A composition as claimed in any preceding claim wherein the composition comprises from 0.01 to 15% by weight of (c).
7. A composition as claimed in claim 2 wherein the cationic polymer (c) has a change in surface tension of less than 15 dynes when measured according to an adsorption test as hereinbefore defined.
8. A composition as claimed in claim 7 wherein the cationic polymer (c) has a change in surface tension of less than 8 dynes when measured according to the adsorption test.
9. A composition as claimed in any preceding claim wherein the contact angle of a drop of water on a surface previously treated with the formulation of Example 2 comprising 0.8% by weight of (c) is less than 10°.
10. A general purpose cleaning composition comprising:
  - (a) 1 to 10% by weight of a nonionic surfactant;
  - (b) 0.25 to 5% by weight of a cationic surfactant which has a sanitising action;
  - (c) 0.1 to 5% by weight of a non-anionic polymer which has an adsorptive affinity to hard surfaces.



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## EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 197 649 (THE PROCTER & GAMBLE CO.) * Page 2, line 12 - page 4, line 23; page 7, lines 14-25; page 8, line 30 - page 9, line 21 * ---	1-3, 5, 6	C 11 D 1/835 C 11 D 3/37
X	CHEMICAL ABSTRACTS, vol. 103, no. 8, August 1985, abstract no. 55735u, Columbus, Ohio, US; & JP-A-60 51 796 (LION CORP.) 23-03-1985 * Abstract * ---	1, 4-6, 10	
X	GB-A-2 164 657 (COLGATE-PALMOLIVE CO.) * Claims 1, 44; page 3, lines 13-25; page 14, table 3, example 5 * -----	1, 2, 4-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 11 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-01-1990	Examiner HILGENGA K.J.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	